An Improved Falling-Film Reactor for Viscous Liquids

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ABSTRACT: This paper presents the design of a sulfonation reactor that is intended for enhanced performance when the viscosity of the liquid phase increases, thus reducing gas–liquid transfer rates. The proposed design allows adequate transfer rates to be maintained by progressively increasing the shear stress exerted by the gas over the liquid film. The effectiveness of the design has been tested in runs in which dodecylbenzene and lauryl alcohol 1.80E are sulfonated/sulfated.

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KEY WORDS: Annular flow, convective transfer, falling film, shear stress, sulfonation, turbulent diffusivity, viscous liquids.

The heat and mass transfer in a falling-film reactor can be seen as comprising several stages. For heat transfer, this means heat generation within the film by the reaction, heat transfer within the liquid phase to the reactor wall and to the gas–liquid interface, heat transfer through the reactor wall, and heat transfer from the liquid phase to the gas phase. For mass transfer, it means transfer between gas and liquid phase, diffusive and convective transfer within the liquid phase, and chemical reaction.

The design presented in this paper pursues an enhancement of reactor performance by influencing mass and heat transfer rates between gas and liquid phases as well as in the liquid phase. The reactor was tested with two reactions: sulfonation of dodecylbenzene (DDB) and sulfation of lauryl ether with an average 1.8 mol ethylene oxide (AES) (DDB, lauryl ether, and ethyleneoxide all from Kao Corporation, Barberá del Valles, Spain). In these reactions, the quality parameters of the final product are: conversion as a percentage by weight of surfactant, free SO_3 in the product, and Klett index (10% active matter in 50:50 ethanol/water, with a 10-mm optical path at 420 nm).

EXPERIMENTAL PROCEDURES

Transfer in falling film. Transfer in a falling film is composed of transfer within each of the phases and transfer between the phases. Transfer between phases is dependent on shear stress exerted by the gas on the liquid, which affects the gas phase transfer coefficient (Kg) (1–3). The higher the shear, the faster the transfer. Transfer within the gas phase can be neglected under industrial conditions, assuming a flat concentration or temperature profile. Finally, transfer within the liquid phase requires consideration of turbulence, including the effect of waves even for laminar liquid flow.

This transfer can be estimated by means of the Yih and Liu model (4). These authors developed a previous model, that of Van Driest turbulent viscosities, which allows calculation of "turbulent" diffusivity coefficients. The tendency is the same as that for gas-phase transfer coefficients, with highly sheared systems with higher transfer rates. Of course, the higher the viscosity of the system, the lower the transfer coefficients within the liquid. This is shown in Figures 1 and 2, in which some runs of the mathematical model (5) were carried out for the sulfonation of DDB. For constant liquid-phase compositions and corresponding turbulent coefficients, it shows how variation of the viscosity in the liquid phase and variation of the shear stress exerted by the gas over the liquid affects the turbulent diffusivity coefficients. As viscosity increases, transfer rates slow down and, if this viscosity is high at the beginning, it will cause the transfer rate to be low from the beginning.

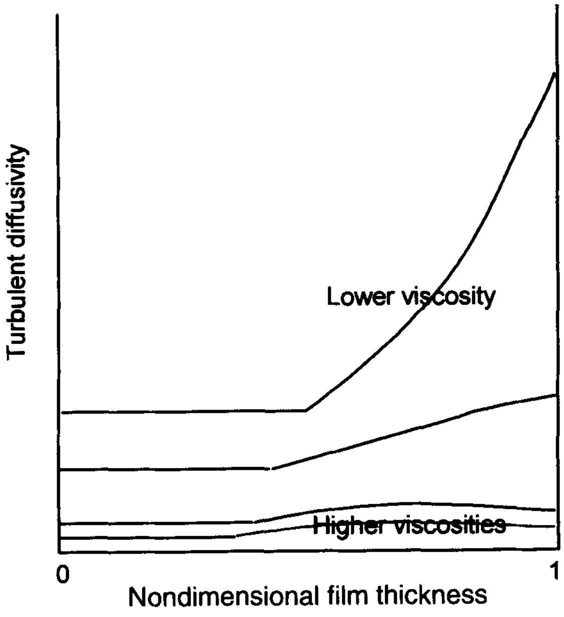

FIG. 1. Turbulent transfer coefficients at various fluid viscosities for constant shear stress.

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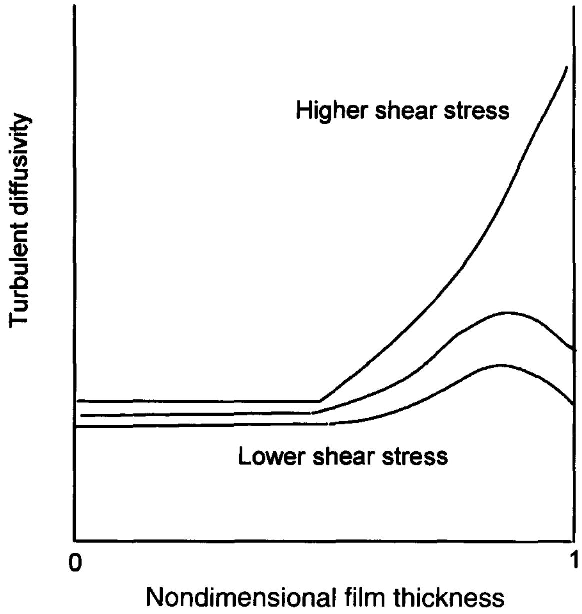

FIG. 2. Turbulent transfer coefficients at various shear stresses for constant viscosity.

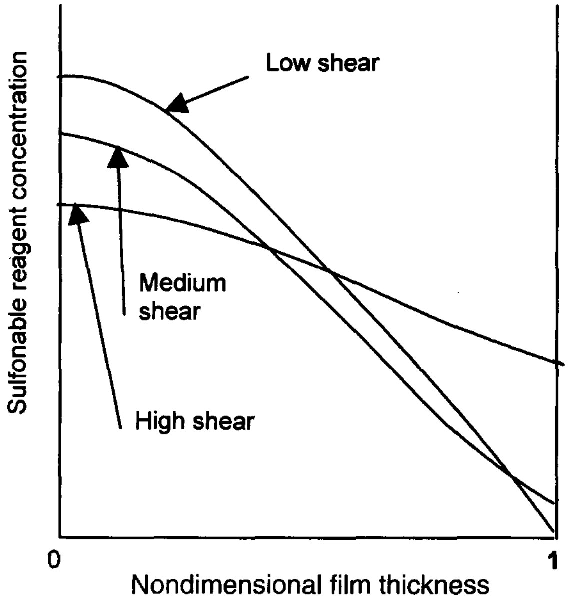

FIG. 3. Radial concentration profile for sulfur trioxide concentration as a function of shear stress (carrier gas flow rate).

Gutierrez *et al.* (5) developed a model for sulfonation of DDB, based on the following hypotheses: (i) Even with laminar flow, convective transfer in the liquid phase should be considered to solve the Fick equation, to take into account the effect of the presence of interfacial waves; (ii) fluid properties (viscosity, density) should be estimated locally to allow numerical solution of microscopic momentum, mass, and heat balance equations; (iii) transfer between gas and liquid phase occurs by physical adsorption. In some previous models (6,7), it was assumed that chemisorption was the transfer mechanism between gas and liquid phases.

With these assumptions, qualitative trends of the performance of falling-film sulfonation were correctly predicted: (i) There is an early shift between control of the transfer process by the gas phase at the beginning of the reaction and control by the liquid phase from then on; (ii) for a constant SO_3/organic molar ratio, the lower the SO_3 molar fraction in the gas (i.e., the higher the carrier gas flow shearing on the liquid), the higher the conversion achieved in the liquid phase; (iii) presence of SO_3 in the liquid was predicted, with higher concentration near the gas–liquid interface and almost zero concentration near the wall (Fig. 3); (iv) the higher the gas shear stress, the lower the concentrations of nonreacted substances. The model predicted that nonreacted liquid reagent had a higher concentration near the wall of the column, far from the gas–liquid interface (Fig. 4); (v) transfer occurs almost completely in a short region at the beginning of the reactor, and overall conversion takes place mainly in that region (as much as 95% of the conversion achieved may take place here).

The results from the model allow us to explain the effect on product quality of factors such as viscosity and surface tension of the liquid phase, and also give the means for a qualitative estimation of color intensity (8,9).

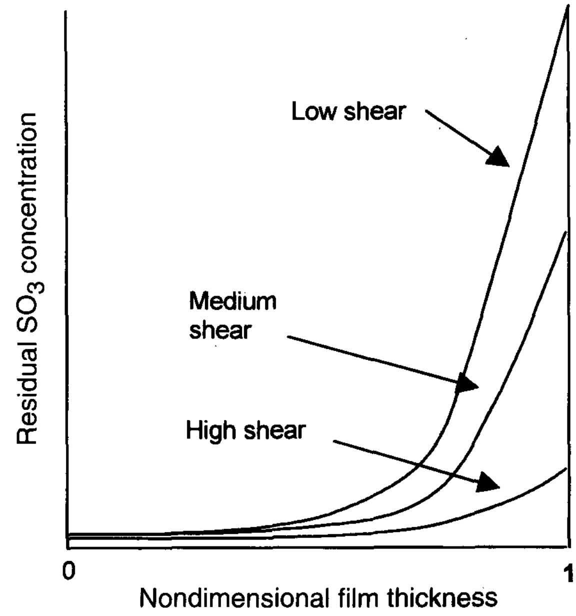

FIG. 4. Radial concentration profile for dodecylbenzene as a function of shear stress (carrier gas flow rate).

It has sometimes been argued that the presence of SO_3 in the liquid phase does not rule out chemisorption as the transfer mechanism because this free SO_3 could be entrained in gas bubbles within the liquid. However, the bubble volume required to keep an amount of trioxide at about 1–2% w/w of the surfactant in the final product (which is a typical content of residual SO_3) would be high. Assuming a pressure of 4 atm and a 10^{-3} SO_3/carrier gas ratio in the entrained gas: (i) Carrier volume entrained would be 0.01 g $SO_3 \cdot$ (1 mol SO_3/80 g

SO_3) • (5.6 l SO_3/mol SO_3) • (1000 $L_{carrier}/L_{SO_3}$) = 0.7 L carrier. (ii) Entraining liquid would be 0.99 g [DDB + dodecylbenzenesulfonic acid (DDBS)] • (0.0011 $L_{DDB + DDBS}$/1 $g_{DDB + DDBS}$) = 0.001098 $L_{DDB + DDBS}$

Thus, the product leaving the reactor would be a form, which is not the case. Therefore, physical absorption is the major mechanism for the transfer of SO_3 to the liquid. These results suggest the following guidelines for handling shear stress in the design of film reactors:

Abrupt increase of shear stress from the beginning will lead to an increase of transfer rates, concentrated near the entry region. This would cause several undesirable effects, such as:

> (i) high heat generation and a marked temperature peak at the initial section of the reactor, which may lead to undesirable effects. (In a sulfation/sulfonation reactor, it would mean thermal decomposition of products or flavoring of undesirable side-reactions, such as dioxane formation, as an adduct of ethoxylated alcohols, and intense coloration of the reaction mixture.); (ii) high initial conversion will lead to a sudden increase in viscosity and, hence, to a slow-down of transfer due to an increase in resistance in the liquid phase; (iii) as a consequence, further gaseous reagent adsorbing on the film will meet strong resistance to diffusion toward unreacted liquid reagent present far from the gas–liquid interface. This would happen because near the gas–liquid interface, the liquid phase would be completely depleted of organic reagent, and then unreacted gaseous reagent would accumulate. This would lead to the presence in the final product of relatively high concentrations of unreacted reagents, both liquid organic and dissolved SO_3, which might affect the quality of the final product.

On the other hand, a progressive increase of shear stress will allow a low initial transfer rate, whose effects will be:

> (i) a relatively low maximum temperature, and a moderate increase of viscosity. Later increases of shear stress counter the growing resistance to transfer in the liquid phase, but not enough to lead to high local conversion rates and heat generation; (ii) further, as transfer rates are kept low along the reactor, accumulation of nonreacted species is also kept low, leading to good product quality.

Following these arguments, an evident choice is a design in which the gas free-flow section is reduced along the reactor so that gas velocity increases and, hence, shear stress on the liquid also increases. In the following section, experimental results are presented that allow quantitation of the improved performance achieved by following this design strategy.

Set-up and tests. The pilot plant (5) consisted of: a falling-film reactor with a water cooling loop with a pump; a reservoir for the liquid reagents kept at 25°C with a pump that feeds the reactor; a syringe pump for the SO_3 feed, which can be alternatively connected to a steel bottle containing sulfur trioxide in a box at 25°C, for recharge, or to a vaporizing vessel during operation; pressure bottles with nitrogen (99.99% pure, less than 0.005 ppm water) to supply the carrier gas that circulates through the vaporizing vessel to drag the sulfur trioxide and pass it to the reactor; and a neutralization tank connected to the liquid outlet of the reactor which was used in sulfation runs. Liquid rates were in the range of 20–100 mL/min. Gas rates were up to 70 nL/min.

The basic reactor, as used for the reference runs (indicated by "No" for shaft length in the tables) is a column of AISI 316L stainless-steel with a length of 2 m and an i.d. of 13.6 mm. The reactor operates in cocurrent downward flow and is cooled by means of a steel jacket which was glued on (welding on the column was avoided during fabrication of the reactor to prevent deformations of the reactor wall). Two heads with gas and liquid reagent inlets and outlets were bolted on.

Prototype design modification of the reactor described above included the placement of a shaft in axial position, connected to the bottom of the reactor (Fig. 5, left) to produce a reduction of the gas flow section at a given distance from the top of the reactor. The central shaft was an AISI 316L stainless-steel tube with an o.d. of 3/16″. Its upper end was sealed, and the lower end was inserted tightly into the gas output conduit (with an i.d. also of 3/16″). Two 5-cm long slots were made along the sides of the shaft near the bottom to allow an exit for the gas flow. Two shafts, 40 and 120 cm in length, were used. A more efficient design would be obtained with successive stretchings (Fig. 5, center) or even a countinuous reduction of the gas flow section (Fig. 5, right). Note that the stretching produced in the gas flow section is only about one seventh of the initial section.

Liquid reagents were technical-grade DDB and lauryl alcohol with an average 1.8 mol of ethylene oxide. Sulfurtriox-

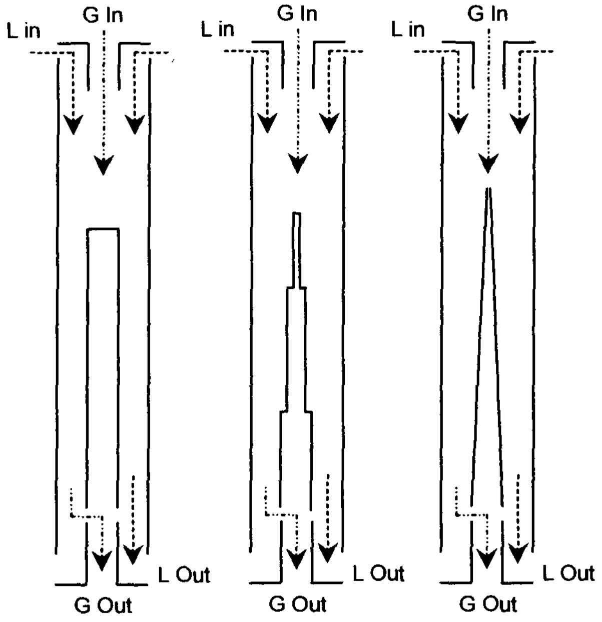

FIG. 5. Schemes for variable section film reactors. A central shaft of adequate shape allows a progressive increase of gas velocity and thus of gas shear stress along the reactor.

ide was stabilized with dimethyl sulfate and supplied by Ugine-Kühlmann (Paris, France). The nitrogen was supplied by SEO Sociedad Española del Oxígeno (San Adrian del Besós, Spain).

The products were analyzed by means of a titration with Hyamine 1622 (Carlo Erba, Milan, Italy), following the ISO 2271-1972 norm, and sometimes color (by absorbance at 420 nm) and free SO_3 (as sulfate) were also analyzed.

Test 1: Effect of liquid flow rate on conversion. Four runs were carried out, with results shown in Table 1. Two reference flow rates for a reactor with a constant gas flow section were assayed, and then two experiments were performed with a variable gas flow section reactor. In the latter, liquid feed rates were 1.5 times higher than the reference rates.

Test 2: Performance improvement regarding color and SO_3 in the final product. In these experiments (Table 2), two liquid flow rates were selected, the same for the two reactors. The carrier gas rate was fixed, and the molar ratio of sulfur trioxide/surfactant was set to 1 for all four experiments.

Test 3. Enhanced performance when dealing with an increase of the viscosity of raw materials. Table 3 shows the results for the sulfation of lauryl alcohol in both reference and variable gas flow section reactors. In the experimental set-up, the operational conditions were chosen to yield good conversion with DDB in the reference reactor.

RESULTS AND DISCUSSION

The conversion values for the modified reactor in test 1 are higher. Furthermore, the higher liquid flow rate for the modified reactor yielded higher conversion than the lower liquid flow rate for the reference reactor. Thus, under the same operating conditions, the liquid flow rate was higher without loss of performance.

The results from test 2 show that the modified reactor works better when operating under conditions that correspond to a poor performance in a reactor with a constant gas flow section. However, when the reference reactor works correctly (i.e., it has good contact and yields good conversion), the variable flow section reactor burns the surfactant and yields a product with too much salt. This occurs because, when the conversion is high at the initial section of the reactor, the increase in transfer in the next flow region leads to excessive accumulation of reagents in the liquid phase, with heat accu-

TABLE 1
Effect of Flow Rate on Conversion[a]

Experiment number	DDB rate (mL/min)	Carrier rate (L/min)	SO_3/DDB	Shaft length (m)	Conv.	SO_3 (% w/w)	Color (Abs.)
1	49	40	1.05	No[b]	81.8	1.0	n.a.
2	32	40	1.05	No[b]	89.1	1.8	n.a.
3	92	40	1.05	0.40	83.7	1.7	n.a.
4	66	40	1.05	0.40	93.0	1.5	n.a.

[a] DDB, dodecylbenzene; conv., conversion; n.a., data not available.
[b] Basic reactor used (see the Experimental Procedures section).

TABLE 2
Performance Improvement in a Variable Gas Flow Reactor[a]

Experiment number	DDB rate (mL/min)	Carrier rate (L/min)	SO_3/DDB	Shaft length (m)	Conv.	SO_3 (% w/w)	Color (Abs.)
5	40	70	1	No[b]	95.4	2.2	0.475
6	70	70	1	No[b]	74.8	0.3	0.202
7	40	70	1	1.20	95.8	2.6	0.774
8	70	70	1	1.20	93.5	0.9	0.062

[a] See Table 1 for abbreviations.
[b] Basic reactor used (see the Experimental Procedures section).

TABLE 3
Enhanced Performance for Highly Viscous Liquids[a]

Experiment number	FAE[a] rate (mL/min)	Carrier rate (L/min)	SO_3/FAE	Shaft length (m)	Conv.	SO_3 (% w/w)	Color (Abs.)
9	25	46	1.1	—	54.2	5.0	n.a.
10	25	46	1.1	0.40	85.5	3.0	n.a.

[a] FAE, fatty alcohol ethoxylate. See Table 1 for other abbreviations.

mulation and local depletion of unreacted liquid reagent near the interphase, thus leaving the incoming sulfur trioxide unreacted.

Test 3 shows the relative ability of the reactors to handle an increase in viscosity. The reference run is poor, whereas conversion is far better with the modificed reactor. Of course, the results do not show good quality for an ethoxylated alkylsulfate, but they are clearly representative of the problems caused when dealing with highly viscous fluids (cethyl alcohol, castor oil).

In conclusion, an improved design of an annular downward film reactor is proposed, which takes advantage of the effect of gas shear stress on gas–liquid transfer and convective liquid transfer. This effect can be used advantageously to reduce liquid-phase resistance to transfer in reactions with increasing viscosity. Moreover, this effect improves contact between reagents in the liquid phase, lowering residual concentrations of unreacted reactants. An operative design can be produced with moderate additional manufacturing expense, due to simplicity of design. In addition, modification of existing reactors to conform to this design would be relatively simple.

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